

N72-33535

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TRANSFORMATION TEMPERATURES  
OF MARTENSITE IN  
BETA-PHASE NICKEL ALUMINIDE

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1. Report No. <b>NASA TM X-2654</b>	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle <b>TRANSFORMATION TEMPERATURES OF MARTENSITE IN BETA-PHASE NICKEL ALUMINIDE</b>		5. Report Date <b>October 1972</b>	
		6. Performing Organization Code	
7. Author(s) <b>James L. Smialek and Robert F. Hehemann</b>		8. Performing Organization Report No. <b>E-7073</b>	
		10. Work Unit No. <b>501-01</b>	
9. Performing Organization Name and Address <b>Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135</b>		11. Contract or Grant No.	
		13. Type of Report and Period Covered <b>Technical Memorandum</b>	
12. Sponsoring Agency Name and Address <b>National Aeronautics and Space Administration Washington, D.C. 20546</b>		14. Sponsoring Agency Code	
15. Supplementary Notes			
16. Abstract Resistivity and thermal arrest measurements determined that the compositional dependence of $M_s$ (martensite start) temperatures for NiAl martensite was linear between 60 and 69 atomic percent nickel, with $M_s = 124 \text{ Ni} - 7410 \text{ K}$ . Resistivity and surface relief experiments indicated the presence of thermoelastic martensite for selected alloys. Some aspects of the transformation were studied by hot stage microscopy and related to the behavior observed for alloys exhibiting the shape-memory effect.			
17. Key Words (Suggested by Author(s)) <b>Nickel aluminide Intermetallic Compounds Martensite Transformation temperatures</b>		18. Distribution Statement <b>Unclassified - unlimited</b>	
19. Security Classif. (of this report) <b>Unclassified</b>	20. Security Classif. (of this page) <b>Unclassified</b>	21. No. of Pages <b>14</b>	22. Price* <b>\$3.00</b>

# TRANSFORMATION TEMPERATURES OF MARTENSITE IN

## BETA-PHASE NICKEL ALUMINIDE

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### SUMMARY

Buttons of the intermetallic compound NiAl were made over the composition range of 60 to 70 atomic percent nickel. Large increases in resistivity with cooling were used to determine  $M_s$  (martensite start) temperatures less than room temperature; while thermal arrests in cooling curves were used to determine  $M_s$  temperatures up to 1200 K. The dependency of  $M_s$  temperatures on composition was given by  $M_s = (124 \text{ Ni} - 7410)\text{K}$ , where Ni refers to atomic percent nickel. From these data no thermally induced martensite should be expected for alloys with less than 60 atomic percent nickel, that is, 10 percent in excess of stoichiometry. The increase in  $M_s$  temperatures with nickel content can be rationalized from both the standpoints of decreasing electronic stability and of decreasing shear constants of the  $\beta$  structure.

Metallographic observation of the continuous growth of martensite plates with cooling and the minimal hystereses in resistivity curves both indicated the thermoelastic nature of the transformation. Reversibility was also documented by the production of reproducible  $\beta$  microstructures with repeated cycling through the transformation. These observations show that ordered nickel-rich NiAl possesses many of the prerequisites for the shape-memory effect, as required by the present theory.

### INTRODUCTION

$\beta$ -NiAl is a 3/2 electron compound having the typical B2 CsCl structure and exists over the composition range of 43 to 70 atomic percent nickel at 1670 K (ref. 1). Unlike most  $\beta$  compounds, NiAl has not been observed to transform martensitically at the stoichiometric composition (ref. 2). However, nickel-rich alloys do decompose in this

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fashion. Maxwell and Grala reported martensitic microstructures for a quenched 68.5 atomic percent nickel alloy (ref. 3), whereas Ball produced stress-induced martensite in a 57 atomic percent nickel alloy (ref. 4). Other stress effects associated with the transformation were observed by Enami and Nenno in a 63.2 atomic percent nickel alloy (ref. 5). Specifically they observed the shape-memory effect in a specimen deformed at room temperature and heated to 543 K, while deformation at 553 K exhibited "super-elastic" behavior. These types of behavior are common for  $\beta$ -compound martensites and have been observed in CuZn, TiNi, AuCd, and Cu-Al-Ni (refs. 6 to 9, respectively) alloys.

Rosen and Goebel observed martensitic microstructures at room temperature for alloys having greater than 63.5 atomic percent nickel (ref. 10). From X-ray diffraction data they described the crystal structure of a 66 atomic percent nickel alloy as  $L1_0$ , a tetragonal distortion of the ordered CuAu I face centered cubic (fcc) structure. The excess of nickel atoms were accommodated on the (001) face centers, where a random distribution of nickel and aluminum atoms was proposed.

Oxidation resistant coatings on nickel-base superalloys currently represent the most widely used commercial application for NiAl. Extended high-temperature service, however, eventually degrades the oxidation resistance of NiAl by diffusion of aluminum into the substrate and in the repeated formation and spalling of a protective  $Al_2O_3$  film. Recently martensite was identified in a NiAl coating on a nickel-base superalloy, which had been depleted of aluminum by 300 hours of cyclic oxidation at 1365 K (ref. 11). The strains associated with the martensitic reaction might contribute to the spalling of  $Al_2O_3$  and thus to the degradation of the coating. The present work reports  $M_s$  (martensite start) temperatures for the nickel-rich compositions of NiAl, which are of interest in the use of NiAl as a protective coating.

## MATERIALS AND PROCEDURE

### Material

NiAl button castings were produced by tungsten arc melting high purity nickel and aluminum (99.99 percent) in an argon atmosphere. Alloys were made over the range of 60 to 70 atomic percent nickel in increments of approximately 1 atomic percent. A double arc melting procedure followed by vacuum annealing near 1670 K for 20 hours was used to improve homogeneity. In spite of these precautions, wet chemical analyses, accurate to 0.4 atomic percent, showed that variations in the nickel content of about 1 atomic percent existed in each of the castings. Unfortunately, chemical analyses could not be obtained for the individual test specimens used for  $M_s$  determinations



because of the small specimen sizes (0.5 by 0.5 by 7 mm) dictated by the testing techniques. Thus it was difficult to obtain a representative value of the compositions.

## Determination of Martensite Start Temperatures

Resistivity, thermal arrest, and microstructural techniques were employed to determine  $M_s$  temperatures. Resistivity measurements were used for alloys with  $77\text{ K} \leq M_s \leq 373\text{ K}$ , and thermal arrests in cooling curves were used for alloys with  $373\text{ K} \leq M_s \leq 1200\text{ K}$ . Microscopic observations of martensitic surface relief were used to check these methods for alloys with  $M_s$  near room temperature (62 to 63 at. % nickel).

The resistivity method consisted of applying a constant current of 0.100 ampere to the NiAl specimen, amplifying the resultant voltage drop, and plotting this against specimen temperature on an X-Y recorder. Any thermal emf across the specimen was averaged out by means of polarity reversing switches. Cooling was accomplished by an alcohol bath immersed in an outer bath of liquid nitrogen. The average rate of temperature change was less than 0.1 K per second. The onset of a resistivity rise due to the transformation was used to determine  $M_s$ . The  $M_s$  temperatures measured by this technique were accurate to  $\pm 5\text{ K}$ .

Cooling curves for thermal arrest tests were obtained by self-resistance heating the NiAl specimen and fast cooling. Temperature was recorded as a function of cooling time by means of a thermocouple spot welded to the specimen surface. The thermal arrest due to the heat of transformation was used to determine  $M_s$ . For this method  $M_s$  temperatures could be determined with  $\pm 5\text{ K}$  accuracy. Alloys having greater than 65 atomic percent nickel contained precipitates of the equilibrium phase  $\text{Ni}_3\text{Al}$ . Therefore, these alloys were first heated to 1670 K to dissolve any  $\text{Ni}_3\text{Al}$ . Air cooling at 1000 K per second (above 1200 K) was fast enough to suppress isothermal transformation to  $\text{Ni}_3\text{Al}$  during thermal arrest testing. There was no change in the  $M_s$  temperature when testing the same specimen in  $10^{-4}$  torr vacuum and then in air. For convenience these tests were subsequently conducted in air.

Observations of surface relief were made on mounted and polished specimens using conventional light microscopy. Simultaneous thermal arrest or resistivity tests showed that the start and finish of the changes in surface relief corresponded within 5 K to the start and finish of the thermal arrests or changes in resistivity. It was concluded that the resistivity and thermal arrest methods were sufficiently accurate for determining  $M_s$  temperatures.

## RESULTS

### Martensite Start Temperatures

Typical voltage drop (i. e., resistivity) curves are shown in figure 1 for a 62 atomic percent nickel NiAl specimen. (Resistance or resistivity could not be calculated because the absolute voltage drop across the specimen was not measured.) On cooling, a large increase in resistivity occurred with the formation of martensite. The  $M_s$  temperature was arbitrarily defined as the relative minimum in the curve, which was 268 K for this specimen. Further cooling to 231 K completed the transformation and normal behavior of resistivity with cooling was resumed. On reheating to room temperature only a small amount of temperature hysteresis occurred.

The composition dependence of  $M_s$  determined from the combined resistivity and thermal arrest data is shown in figure 2. The data points are the average measurements of at least three specimens for each composition, and the error bars indicate the spread in  $M_s$  temperatures. This spread was caused largely by variations in composition from specimen to specimen of a given casting. Difficulty was encountered in obtaining  $M_s$  for the 60.8 and 69.2 atomic percent nickel specimens. The 60.8 atomic percent nickel casting was contaminated with tungsten during arc melting which sup-

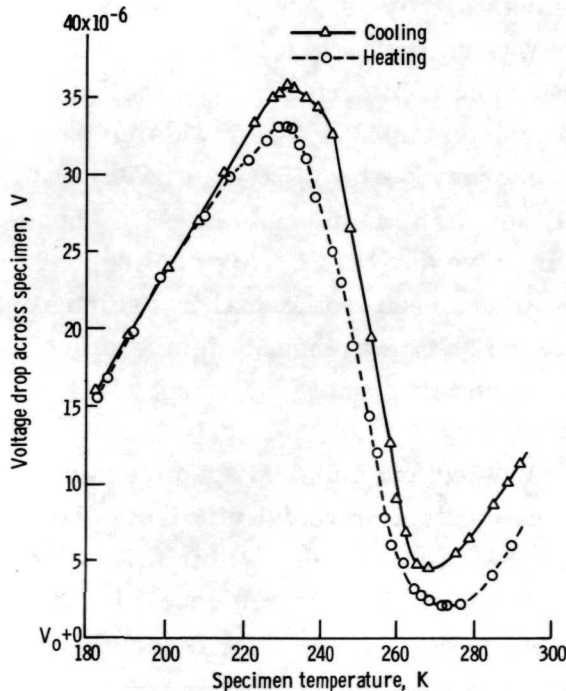


Figure 1. - Temperature dependence of resistivity for a 62 atomic percent nickel NiAl specimen.

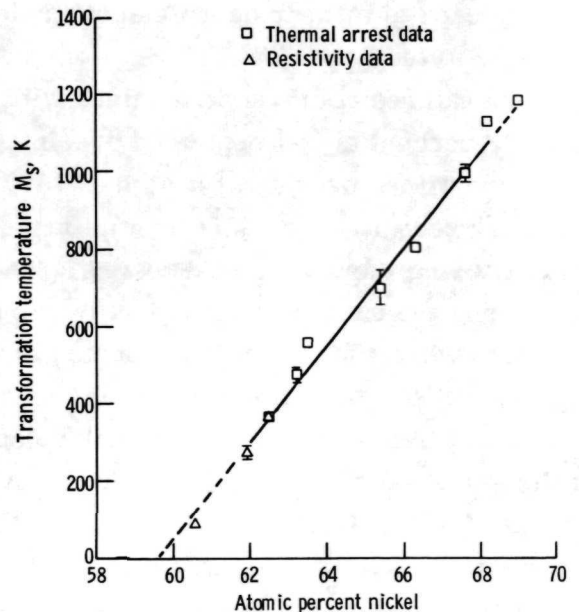


Figure 2. - Compositional dependence of transformation temperatures for NiAl martensite.

pressed the transformation for some specimens. The dissolution temperature of  $\text{Ni}_3\text{Al}$  for the 69.2 atomic percent alloy was very close to the melting temperature for this alloy. Therefore it was difficult to dissolve all the  $\text{Ni}_3\text{Al}$  without melting.

On the basis of the 40 other specimens tested, a least squares analysis of the data yielded the relation:  $M_s = (124 \text{ Ni} - 7410)\text{K}$ , where Ni refers to atomic percent nickel. A high regression coefficient was obtained ( $r^2 = 0.98$ ), which indicated that a linear function described the relation well. Data from both the slow-cooling resistivity tests and the fast-cooling thermal arrest tests fell on the same curve.

## Microstructural Characteristics of the Transformation

A martensitic specimen ( $M_s \approx 360 \text{ K}$ ) of the 62.7 atomic percent nickel alloy was mounted in epoxy and polished metallographically. Transformation to  $\beta\text{-NiAl}$  by self-resistance heating resulted in the formation of surface relief by the reverse martensitic shear formation. The sequence of photomicrographs in figure 3 shows the progression of the martensite  $\rightarrow \beta$  transformation as a succession of advancing wedges.

Subsequent cooling caused the formation of new martensitic surface relief presumably caused by a changing stress state on the specimen. (This new relief could not have been due to untransformed  $\beta$  because it was not removed by cooling to 77 K, 300 K below  $M_s$ .) This new martensitic relief could be changed by repeated cycling through the transformation temperature, whereas the same  $\beta$  relief markings were obtained for every cycle (fig. 4). This reproducibility of the  $\beta$  structure occurred for all areas examined, even after many cycles through the transformation.

The transformation is shown in greater detail in the sequence of photomicrographs in figure 5. Figure 5(b) shows the lateral growth of two martensitic plates marked X and Y. Using the crack as a reference, it is evident that plate Y grew at the expense of plate X, again presumably because of a changing stress state on the specimen. The relief markings were also observed to travel in a continuous manner with changes in temperature.

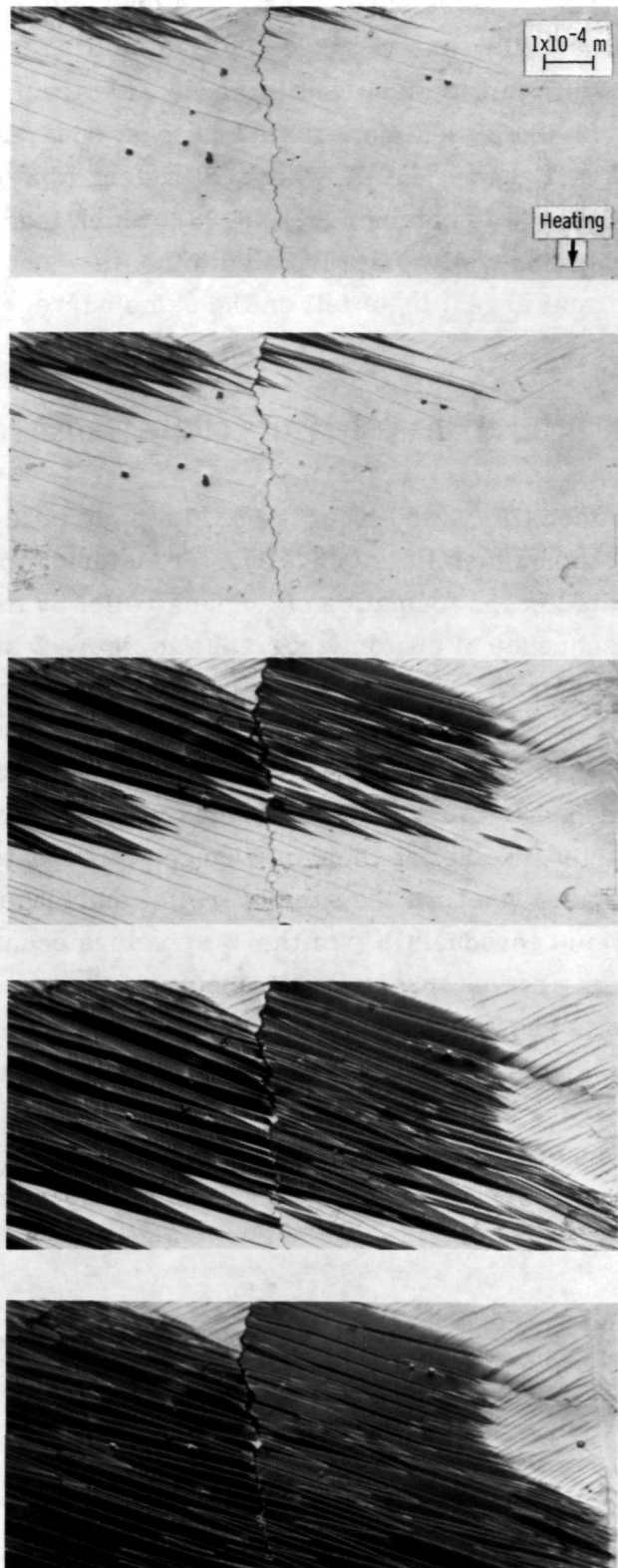
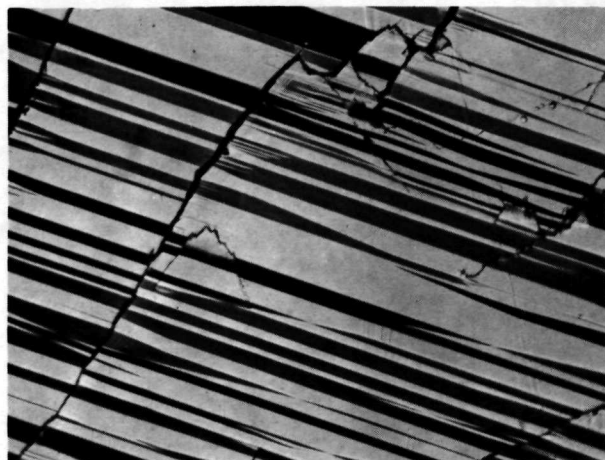


Figure 3. - Formation of surface relief while heating a martensitic 62.7 atomic percent nickel alloy. X60.

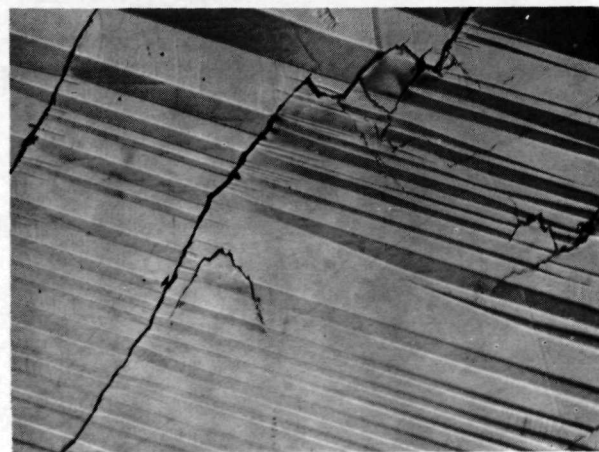
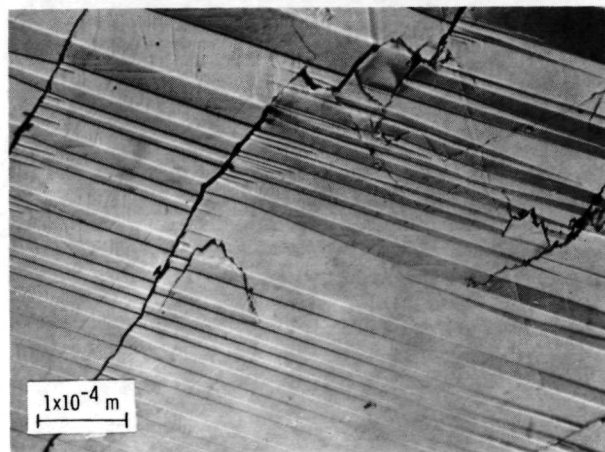


Second cycle

Fourth cycle



(a) Martensitic relief.

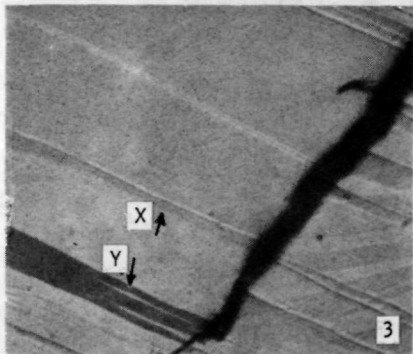
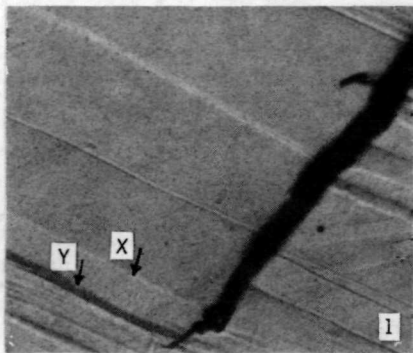


(b)  $\beta$  relief.

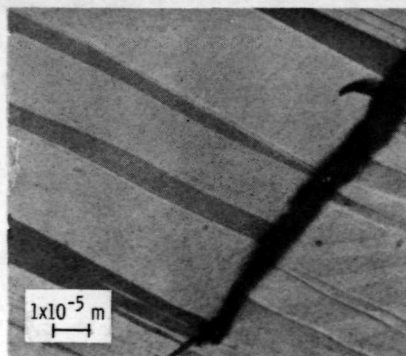
Figure 4. - Reproducibility of  $\beta$  surface relief structures after repeated cycling of 62.7 atomic percent nickel alloy. X120.



(a)  $\beta$  relief.



(b) Cooling to martensite.



(c) Transformation to martensite complete.

Figure 5. - Sequence of relief structures showing progress of martensitic reaction in 62.7 atomic percent nickel alloy.

## DISCUSSION

### Compositional Dependence of Martensite Start

The major conclusions to be drawn from the compositional dependence of  $M_s$  temperatures in figure 2 are (1) that a large deviation from stoichiometry ( $\sim 10$  at. %) is needed before thermal martensite can be formed and (2) that a large increase in  $M_s$  temperatures occurs with increasing nickel content. Ball previously discussed the role of nonstoichiometry in producing martensite in NiAl in terms of  $\beta$  stability and its resistance to shear (ref. 4):

By increasing the nickel content the electron to atom ratio,  $e/a$ , of the electron compound is decreased from its ideal value of  $3/2$  at stoichiometry. This decreases the stability of  $\beta$  with respect to the martensitic structure and thus rationalizes the tendency to transform to martensite at successively higher temperatures. Equivalently, increasing the nickel content can be said to decrease the strong ordering forces between nickel and aluminum atoms. This in turn reduces the resistance of  $\beta$  to the shearing needed for martensitic reactions, thus, again rationalizing the tendency to transform at successively higher temperatures. No martensite is formed in stoichiometric alloys because of the high value of the shear constant relative to other  $\beta$  compounds.

At this time it appears that low values of the shear constant (or high values of the elastic anisotropy for  $\beta$  compounds) is the factor that most reliably predicts the occurrence of martensitic reactions (refs. 12 and 13). Some success had been previously obtained in correlating increasing  $M_s$  temperatures with decreasing  $e/a$  ratios (refs. 14 and 15) (as is the case in this study), but more detailed studies of ternary compounds showed that this trend was not always followed (refs. 12, 16, and 17).

## MICROSTRUCTURES

The transformation in NiAl has many of the characteristics common to thermoelastic martensites of ordered  $\beta$  compounds - small hysteresis, reversibility, and anelastic behavior. The small hysteresis evidenced by both resistivity and surface relief observations is considered direct proof of the thermoelastic nature of the transformation.

The reversibility, that is, the transformation of martensite plates back to the original  $\beta$  crystal, was revealed by the reproducible  $\beta$  relief structures obtained. Usually samples are polished in the  $\beta$  condition, and reversibility is demonstrated by transforming to martensite, then back to a plane surface of the original  $\beta$  crystal. In this study samples were polished in the martensitic condition. Consequently the  $\beta$  structure

obtained by subsequent heating contained relief markings due to the reverse transformation. Thus reproducible  $\beta$  relief structures implied reversibility. (The observation that the  $\beta$  relief striations had a one-to-one correspondence with some of the plate boundaries of etched martensite indicated that the striations were caused simply by reverse shearing and did not represent individual "plates" of  $\beta$  of different orientations.)

The growth of one martensitic plate into another (shown in fig. 5) is suggestive of "ferroelasticity" and "shape-memory" (ref. 7) effects. These types of anelastic behavior both entail either the stress-induced growth of martensite of one orientation at the expense of that of another or the conversion of one twin orientation to another. In describing the shape-memory effect in NiAl, Enami and Nenno showed that sufficient stress indeed caused a change in the orientation of all the martensite present (ref. 5).

Recently, the characteristics of the shape-memory effect for  $\beta$ -compound martensites were reviewed (ref. 18). It was stated that there are three prerequisites for this phenomenon to occur: the transformation must be thermoelastic, the parent and martensite phases must be ordered, and the martensite must be internally twinned. The present study and previous work (ref. 10) have documented the first two conditions for NiAl, however, the internal substructure has not yet been studied. It was also indicated that the memory effect observed on heating is caused by the transformation back to the original parent phase. Thus the reproducible parent structures obtained from various martensitic structures in the present work suggest that the memory effect should indeed occur by the martensite-parent phase reaction for NiAl.

The memory temperature or  $\beta_s$  (predicted from this work) for the 63.2 atomic percent alloy studied by Enami and Nenno is approximately 430 K. (This assumes that  $\beta_s \approx M_s$  for thermoelastic martensites, as indicated by the resistivity curves in fig. 1.) Their observation of the memory effect at 543 K and not at 430 K, can possibly be accounted for by the aforementioned uncertainties in composition ( $\sim 1$  at. %). Yet their observation of martensitic microstructures at 773 K is a significant departure (340 K or 3 at. %) from the data reported herein. Their observation also contradicts the theory which states that the memory effect is a result of the transformation to  $\beta$  (ref. 18). With the information available there is no simple explanation of this discrepancy.

## X-Ray Diffraction

A limited amount of X-ray diffraction work was performed to distinguish the martensite phase from the  $\beta$ -NiAl or  $\gamma'$ -Ni<sub>3</sub>Al phases. Debye-Scherrer patterns for large grained 63.7- and 67.8-atomic-percent nickel NiAl filaments showed a reasonable correlation to the face centered tetragonal (fct) patterns obtained for 66-atomic-percent nickel NiAl martensite by Rosen and Goebel. Because of the large grain size, the



patterns were spotty, and these spots showed considerable streaking between the Debye rings. These streaks could be due to stacking faults. This suggests that NiAl martensite may have some resemblance to the heavily faulted structures (as evidenced by streaked electron diffraction spots) of many  $\beta$ -compound martensites. These structures are based on stacking sequences of the same fcc CuAu I structure and were observed for Cu-Al (ref. 19), CuZn (ref. 20), and AuCd (ref. 21) martensites. However, attempts to fit the patterns obtained for NiAl martensite to some of the more common martensite structures were unsuccessful.

## SUMMARY OF RESULTS

Resistivity and thermal arrest tests determined that the compositional dependence of  $M_s$  temperatures for NiAl martensite was linear, with  $M_s = (124 \text{ Ni} - 7410)\text{K}$ . Extrapolation to absolute zero showed that no thermally induced martensite should be expected for alloys with less than 60-atomic-percent nickel, that is, 10 percent in excess of stoichiometry.

The documentation of reversibility and the thermoelastic nature of the transformation showed that ordered NiAl martensite possesses many of the prerequisites for the shape-memory effect, as required by the present theory.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, September 1, 1972,  
501-01.

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